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77 WT % CaF_2 - 23 WT % LiF FUSED TO IN-750 ALLOY

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SUMMARY

A coating composed of 77 wt % CaF_2 - 23 wt % LiF fused on IN-750 nickel-based alloy was studied using SEM, XRD, EDX, and optical microscopic methods. The surfaces examined were the as-fused coating with no subsequent treatment, the coating after ultrasonic cleaning in water, and the uncoated polished and etched metal. It was found that the coating reacts during fusion with Ti and Nb rich inclusions in the alloy. Numerous small rectangular crystallites of $\text{Ca}(\text{Ti},\text{Nb})$ oxide are formed beneath an overlay of fused fluoride composition. These crystallites are stubby and appear to be embedded in the metal substrate surface. It is known from previous studies that this coating-alloy system has good tribological properties in extreme conditions, such as liquid fluorine. It has been concluded from the present study that the short firmly embedded crystallite protuberances contribute to the coating adherence and thereby to enhanced coating wear life.

INTRODUCTION

Solid lubrication in extreme environments as cryogenic liquid fluorine and hydrogen on the one hand and high temperature air on the other require nonreactive materials. Material combinations must be selected that will be compatible with these very reactive environs during sliding contact and will also provide the low wear and friction necessary. It has been shown (refs. 1 to 4) from thermodynamic calculations that Ca and Li fluorides, among other fluorides of group I and II elements, should be nonreactive in oxygen, hydrogen, and sodium and they would be expected to be stable in fluorine because they are fully fluorinated. One such system tested (refs. 1 to 4) was a fused composition of CaF_2 and LiF applied to a Ni-based superalloy. This coating was composed of 77 wt % CaF_2 and 23 wt % LiF . This coating provided good sliding lubrication in liquid fluorine (refs. 1 to 3).

Results of a study of the above coating in the un-tested condition using SEM, XRD, EDX, and optical microscopic means are reported herein. The use of these tools provided a description of the morphology and composition of the coating phases resulting from its interaction with the metal substrate and atmospheric components present during preparation.

EXPERIMENTAL

The coating was composed of 77 wt % CaF_2 - 23 wt % LiF and was applied to IN-750 alloy. The coated specimens studied were prepared by a procedure previously described in references 3 and 4. Briefly, a water suspension of the

coating materials was sprayed on the surface of the IN-750 preheated to 60 °C. This was then fused at 900 °C in a hydrogen atmosphere furnace for 15 min. The hydrogen contained 20 to 30 ppm of water. After fusion the coatings were 0.0025 to 0.005 cm (0.001 to 0.002 in.) thick.

XRD, SEM, EDX, and optical microscopic studies were made of the as-fused, un-tested coating surface, the coating surface after ultrasonic cleaning in water, and the uncoated IN-750 alloy. To minimize charging of the as-fused coating surface in the SEM a thin sputtered gold layer was applied. All SEM photographs are secondary electron images.

Ultrasonic cleaning was accomplished by placing the sample in a beaker of distilled water at room temperature for 30 min. This process removed the water soluble material and exposed areas of the underlying structures. The material primarily removed was LiF which has an appreciable water solubility of 0.27 g/100 g of water at 20 °C compared to CaF_2 with a solubility of only 0.0016.

Examination of the uncoated IN-750 alloy was facilitated by sectioning a metal disk and mounting in epoxy then metallurgically polishing and etching.

IN-750 is a Ni-based alloy and has a nominal composition in weight percent of: 15Cr, 6.8Fe, 2.5Ti, 0.9Nb, 0.8Al, 0.7Mn, 0.3Si, and the balance is nickel.

RESULTS AND DISCUSSION

A phase diagram of the CaF_2 -LiF binary coating system (ref. 5) is presented in figure 1. This system forms a simple binary eutectic. The eutectic temperature is 769 °C. Below this temperature the components are solid, but, above the eutectic temperature a liquid phase is present and changes in amount and composition with rising temperature. The diagram gives compositional and physical state information for the binary system at equilibrium. It is estimated that the actual fusion of the coating was carried out slowly enough to attain near equilibrium compositions.

The initial composition of the unheated coating is composed of 77 wt % CaF_2 - 23 % LiF and is represented by the vertical line in figure 1 at this composition. The liquidus temperature of this composition is 1065 °C and at this temperature 100 percent liquid is present.

A brief discussion of the heating of the coating composition will be made. Up to the eutectic temperature the system is solid. At the eutectic temperature the system is composed of a 59 wt % eutectic liquid phase, which consists of 43 wt % CaF_2 and 57 wt % LiF, in equilibrium with 41 wt % of solid CaF_2 . As the temperature of the coating rises, the CaF_2 content increases in the liquid phase which is in equilibrium with the remaining solid CaF_2 . Finally at the fusion temperature of 900 °C there is 71 wt % of liquid phase composed of 60 wt % CaF_2 and 40 wt % LiF in equilibrium with 29 wt % solid CaF_2 . On cooling down after fusion the above processes are reversed because fused fluoride salt systems crystallize rapidly compared to the slow cooling rate of the comparatively massive alloy test specimen substrate.

The firing or fusion temperature of 900 °C was intentionally chosen to be above the melting point of the eutectic but below the liquidus temperature for the coating composition. The presence of solid CaF_2 dispersed throughout the liquid phase reduces the spreading rate of the melt and thereby enables even vertical surfaces to be covered with coating at least 0.003 cm thick.

Figure 2 is a SEM image of the fused coating surface. This is the surface which has been reported to provide good friction and wear (refs. 1 to 3) in liquid fluorine. It is a very globular structure. This type of structure is indicative of limited wetting of the substrate which may be the result of incomplete solution of CaF_2 . The solid CaF_2 particles are logical nucleation sites for crystallization of the molten phase during resolidification and although molten fluorides readily wet nickel alloy surfaces, preferential wetting of the CaF_2 nuclei is to be expected. XRD of this surface revealed CaF_2 and LiF as the major components with some smaller amount of LiNiO_2 . It is interesting to note that the valence of the Ni in the lithium nickel oxide compound is +3, this requires locally oxidizing conditions for its formation. The latter compound was probably formed during fusion by reaction of the nickel in the alloy with traces of water vapor in the hydrogen fusion atmosphere and molten LiF . The face centered cubic structure of the substrate alloy was also detected. Detection of the alloy further indicates that the coating between globules is too thin to completely absorb the x-rays. Spot EDX analysis of the dark pit areas between the globules revealed high alloy element concentrations and very low to no Ca. Similar analysis of the globular features showed very high Ca concentrations and no alloy elements and the small rectangularly shaped grains located on the surface of the globules were very high in Ni which indicates they are the LiNiO_2 phase detected in the XRD analysis.

Based on the fact that LiF has a moderately high solubility in water it was decided to ultrasonically treat the coating in water to remove at least some of the fused fluoride and then examine the resulting surface. This revealed an interesting under-structure not visible before the ultrasonic treatment. Figure 3 is an SEM image of this surface. Many small square to rectangular shaped crystallites with flat or hipped roofs are plainly visible on the surface. These features appear to be protruding. Spot EDX analysis shows these features to have a high concentration of Ca, Ti, Nb, and oxygen and no detectable fluorine or carbon. Analysis of spot B which is an area between the crystallites was rich in alloy elements and both Ca and F were not detected. It was estimated from light microscopy that on the average the crystallites are 6.3 μm in height which is small compared to the overall coating thickness of 25 to 50 μm . These crystallites are 6 by 6 μm in size and have a population of 57 000/ cm^2 . These crystallites represent an average 2 percent area coverage of the surface. The conclusion is the crystallites are a water insoluble $\text{Ca}(\text{Ti},\text{Nb})$ oxide. XRD analysis of the washed surface detected $\text{Ca}_3\text{Ti}_2\text{O}_7$, CaF_2 , several unidentified lines and the substrate alloy. This information confirms the presence of calcium titanate crystallites. The unidentified lines may be due to phases as $\text{Ca}_x(\text{Ti},\text{Nb})_y\text{O}_z$.

It appears that the crystallites are higher in Ti and Nb content than would be expected from the overall alloy content of 2.5 Ti and 0.9 Nb. It was difficult to conceive a reaction mechanism for the formation of these crystallites. Two mechanisms suggested themselves. The first involves the preferential solution of Ti and Nb from the uniformly distributed alloy

elements by the fused fluoride followed by nucleation and crystal growth on cooling. The other and possibly more plausible, is reaction of the fused fluoride with areas richer in Ti and Nb than the alloy in general such as intermetallic or carbide inclusions formed in the alloy during precipitation hardening. This dictated a study of the uncoated alloy to determine if areas of high Ti and Nb concentration existed. A piece of the coated alloy was sectioned so as to expose an uncoated surface. This was polished and etched to bring out the alloy microstructure. Figure 4 shows an SEM image of the uncoated, polished, and etched IN-750 alloy. It was found that many inclusions were present in the alloy mostly along grain boundaries. Spot EDX analysis are also presented in figure 4. Study of the data from inclusions A, B, and C reveals they are especially rich in Ti and Nb compared to the alloy grain at spot D. An EDX line scan for Ti, Nb, Cr, Fe, and Ni across one of the larger inclusions is presented in figure 5. These results show that the distribution of Ti and Nb across this inclusion is not uniform, Nb is more concentrated at the edges of the inclusion with Ti highest in the center and very low amounts of Fe, Cr, and Ni.

The observation that the Ti and Nb are more concentrated in small inclusions lead to the conclusion that the $\text{Ca}(\text{Ti},\text{Nb})$ oxide crystallites are formed at the metal surface by reaction with the CaF_2 and an oxygen source. The oxygen source is mainly the water vapor in the hydrogen fusion atmosphere and some smaller amount from oxides on the metal surface. The liquid phase formed during fusion acts to transport the water vapor to the alloy surface.

The following schematic reaction is proposed:



It is estimated that the inclusion population in the metal is $295\,000/\text{cm}^2$. The inclusions range in size from as large as $10\,\mu\text{m}$ in diameter down to less than $1\,\mu\text{m}$ in size. Only 57 000 crystallites are formed per square centimeter this suggests that not all inclusions react or that each crystallite is made up of several inclusions. If the latter is true then each crystallite would contain on the average 5 inclusions ($295\,000\text{ inclusions}/\text{cm}^2$ divided by 57 000 crystallites formed per square centimeter).

Consumption of the CaF_2 with the loss of fluorine in the formation of the crystallites decreases the CaF_2 content of the fused, globular fluoride overcoat to a slight extent. Therefore, the final fluoride overlay coating is not the same as that originally applied but should be richer in LiF. However, some LiF was consumed in the formation of the LiNiO_2 phase during fusion.

Figure 6 is a schematic diagram summarizing the morphology and compositional information for the fused fluoride coating. A stylized presentation of both the cross section and top surface are shown. It is clear that the overall structure is one of short stubby crystallites growing from the alloy surface and covered by a fused fluoride coating.

CONCLUSIONS

A summary of the major conclusions are:

1. The 77 wt % CaF_2 - 23 LiF coating components react with Ti and Nb rich inclusions in the alloy during the fusion in a hydrogen-water vapor atmosphere to form many short $\text{Ca}(\text{Ti},\text{Nb})$ oxide crystals embedded in the surface of the alloy. These crystallites are on the average $6.3\text{ }\mu\text{m}$ in height and covered about 2 percent of the surface area.

2. A fused CaF_2 -LiF overcoating of 25 to $50\text{ }\mu\text{m}$ thickness is present which contains LiNiO_2 crystallites.

This coating structure has proven to possess desirable friction and wear characteristics, therefore, a simple tribological scenario to explain this will be constructed. In sliding contact it is easy to imagine that the stubby crystallites may contribute to increased adhesion and load bearing capabilities of the fused fluoride coating. This premise is based on the fact that the crystallites are so thin and short and appear to be firmly embedded in the metal that even with only moderate strength they could carry a moderate sliding load without fracture. The compressive strength of CaTiO_3 is reported to be 10 to 20 000 psi (69 to 138 MPa) for sintered material 75 to 91 percent dense (ref. 6). The well formed crystallites in this coating could have much higher strength. Also these protuberances could prevent the fluoride from being easily scraped from the surface by providing dams to such action, in effect pinning the globular fluoride to the surface. The penned up fluorides then could provide a continuous solid lubricant to the rubbing top surfaces of the crystallites. Local frictional heating of the fluoride could produce some liquid phase lubrication.

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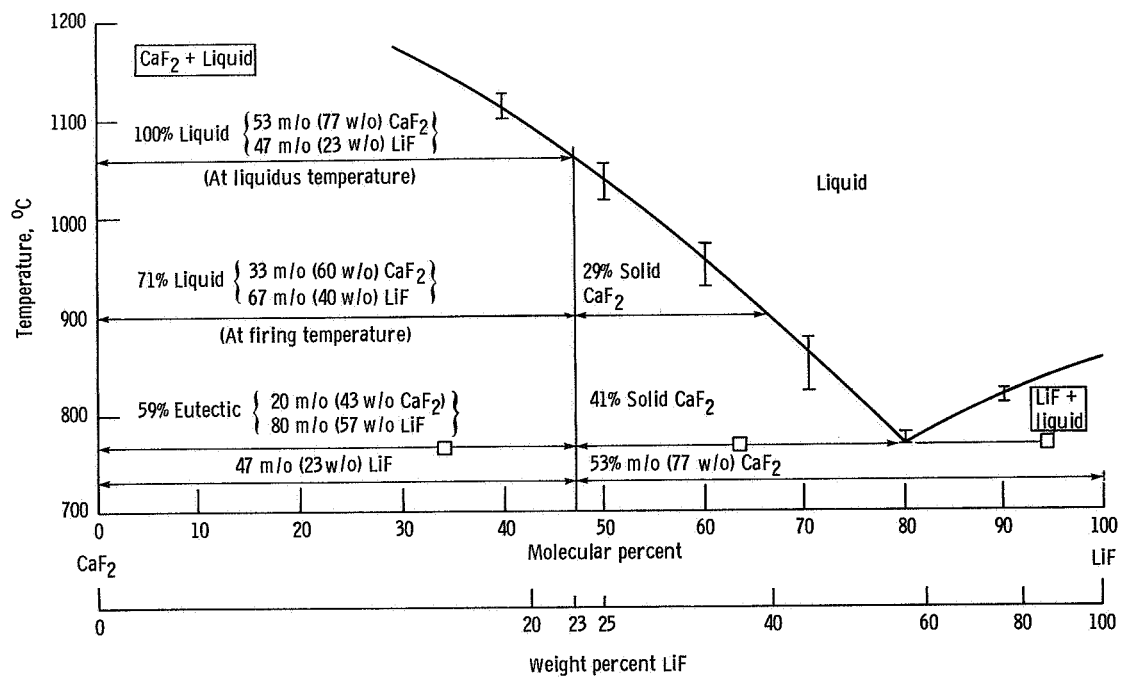


Figure 1. - Phase diagram for the CaF_2 - LiF binary system (ref. 5). Featuring equilibrium compositions at a temperature below the eutectic temperature, at the eutectic temperature, at the fusion temperature and the liquidus temperatures.

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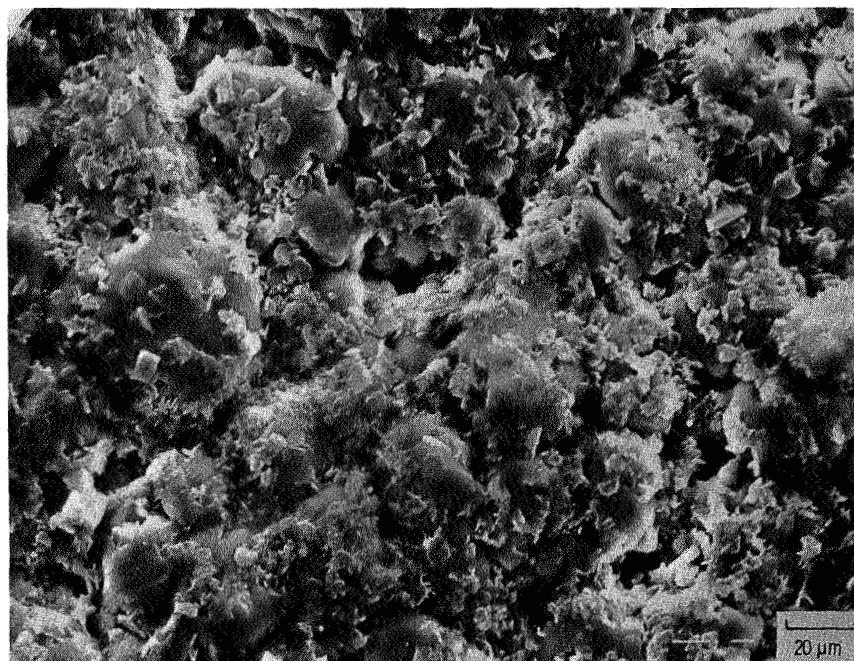


Figure 2. SEM photograph of the coated surface before water washing. (Au coated)

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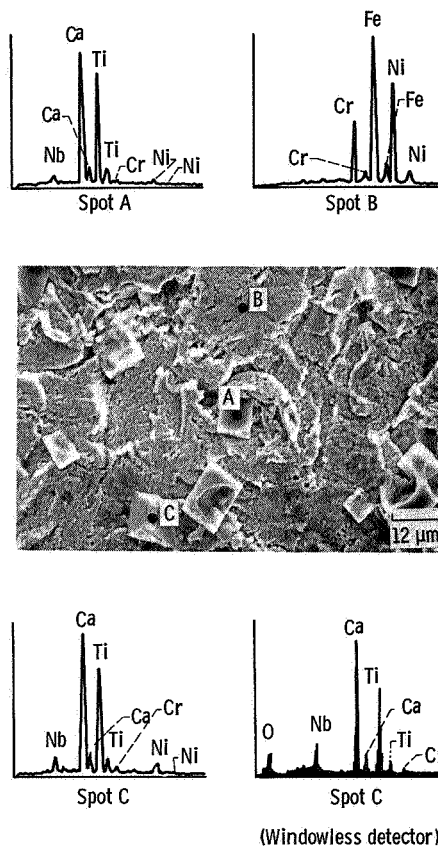


Figure 3. - SEM photograph and spot EDX spectra for the coating surface after water washing.

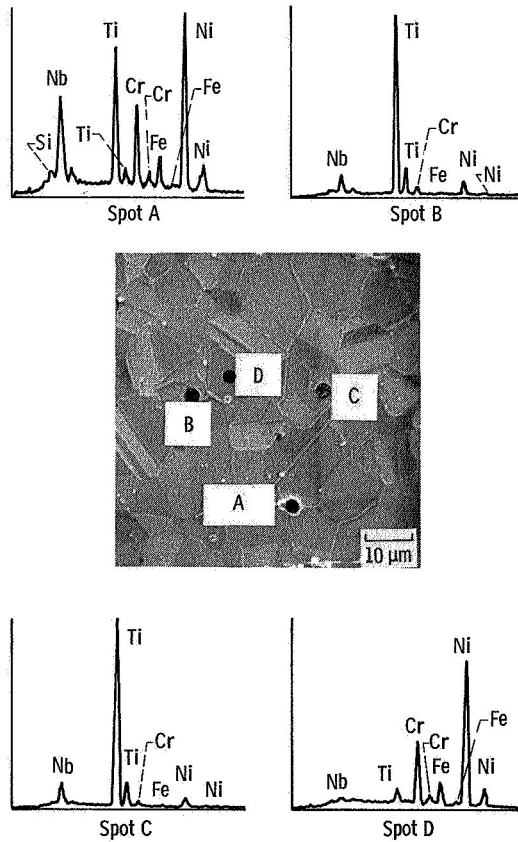


Figure 4. - SEM photograph and spot EDX spectra of the polished and etched uncoated surface of IN-750 alloy.

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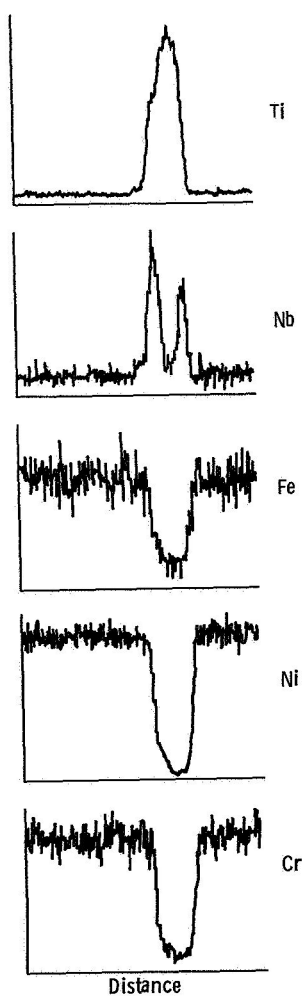
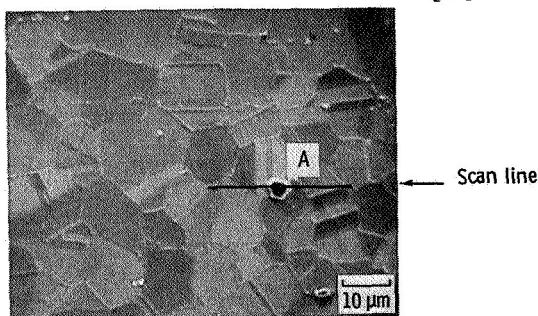


Figure 5. - SEM photograph and digital EDX line scan across feature A for uncoated polished and etched IN-750 alloy.

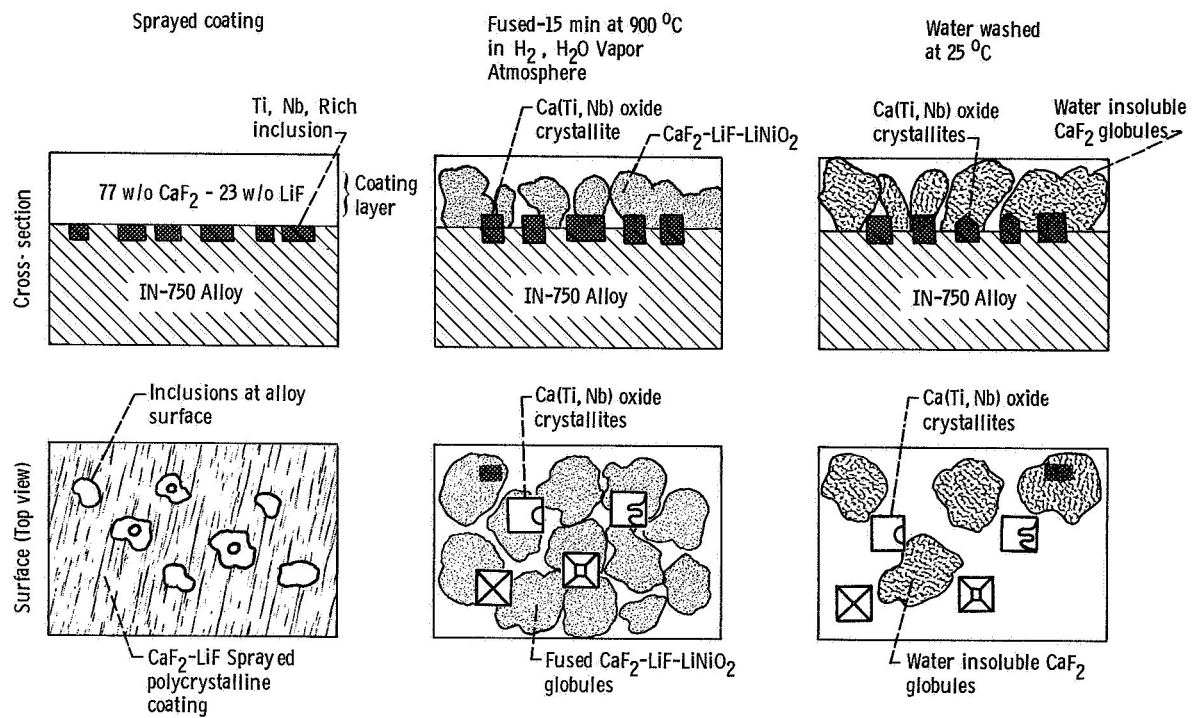


Figure 6. - Schematic diagram of the CaF_2 -LiF coating on IN-750 alloy.

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